

I claim:

1. ~~A~~ heat stabilizing composition for a polyolefin, comprising: (A) an oxidized, non-cationized, non-silylated sulfur black pigment, (B) a hindered phenolic antioxidant, (C) a sulfur-containing secondary stabilizer, and (D) a hindered amine.

2. The heat stabilizing composition of claim 1, wherein (A) is selected from C. I. Sulphur Black 1; C. I. Sulphur Black 2; C. I. Sulphur Black 11; and C. I. Sulphur Black 18.

3. The heat stabilizing composition of claim 1, wherein (A) is present in the range from 0.1 to 10 w% on total wt%., (B) is from 0.01 to 1 w% on total wt.%, (C) is from 0.02 to 2 w% on total wt%, and (D) is from 0.05-1 w% on total wt%.

4. The heat stabilizing composition of claim 1, wherein said sulfur black pigment is washed to reduce the water soluble salts present in said sulfur black pigment.

5. The heat stabilizing composition of claim 1, wherein said phenolic antioxidant is selected from 2,6-di-t-butyl-4-methylphenol;

2,6-di(α -methylbenzyl) 4-methylphenol;

4-hydroxymethyl-2,6-di-t-butylphenol;

butylated hydroxyanisole;

2,6-bis(1,1-dimethylethyl)-4-methyl phenol ;

2-t-butyl-1,4-benzenediol;

octadecyl 3,5-di-t-butyl-4-hydroxybenzyl phosphonate;

ethylene 3,3-bis(3-tert-butyl-4-hydroxyphenyl) butyrate ;

2,2'-methylenebis(4-methyl-6-t-butylphenol);

2,6-di-tert-butyl-4-methylphenol;

2,6-di-tert-butyl-4-hydroxymethylphenol;

4,4'-butylidenebis[3-methyl-6-tert-butylphenol] ;
 2,2'-butylidenebis[4-methyl-6-tert-butylphenol];
 4,4'-methylenebis(2,6-di-tert-butylphenol);
 2,2'-methylenebis (4-methyl-6-nonylphenol);
 2,2'-methylenebis [4-methyl-6-(1-methylcyclohexyl)phenol];
 2,2'-bis(4-hydroxy-3-methylphenyl) propane;
 2,2'-oxalyldiamidobisethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate;
 2,2'-methylenebis(4-ethyl-6-tert-butylphenol);
 2,2'-methylenebis[6-(1-methylcyclocyclohexyl)-p-cresol];
 4,4'-thiobis(6-t-butyl-o-cresol);
 2,2'-thiobis[4,6-di-tert-butyl-m-cresol];
 2, 2'-thiobis[4,6-di-tert-butyl-o-cresol] ;
 4,4'-thiobis (3-methyl-6-t-butyl phenol);
 thiobisdiethylenebis(3,5-di-t-butyl-4-hydroxy)hydrocinnamate;
 butyric acid, 3,3-bis(3-t-butyl-4-hydroxyphenyl) ethylene ester;
 2,2'-ethylidenebis(4,6-di-t-butylphenol);
 2,2'-thiobis(4-methyl-6-tert-butylphenol);
 bis[4-(2-phenyl-2-propyl)phenyl] amine;
 N,N-dimethyl(3,5-di-tert-butyl-4-hydroxybenzyl) amine;
 4,4'-di-tert-octyldiphenylamine;
 1,1-bis(2-hydroxy-3,5-dimethylphenyl)-3,5,5-trimethylhexane; and
 1,6-hexamethylene bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] .

the polyphenols, like 1,3,5-tris(4-t-butyl-3-hydroxyl-2,6-dimethylbenzyl)-1,3,5-
 triazine-2,4,6-(1 H, 3H, 5H)-trione;
 tetrakis[methylene (3,5di-t-butyl-4-hydroxy)hydrocinnamate]methane;
 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-s-triazine-2,4,6
 (1H, 3H, 5H)-trione;
 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate;
 trimethyl-2,4,6-tris(3,5,-di-t-butyl-4-hydroxybenzyl)benzene);
 tris(3,5,-di-t-butyl-4-hydroxybenzyl) isocyanurate;

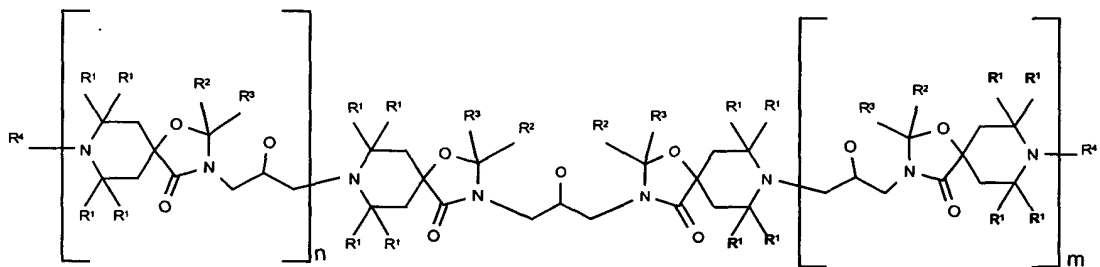
tris(3,5-di-tert-butyl-4-hydroxyphenyl) phosphate;
 hydrocinnamic acid, 3,5-di-t-butyl-4-hydroxy-, triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6-(1H, 3H, 5H)-trione;
 1,1,3-tris ((2-methyl-4-hydroxy-5-t-butylphenyl)butane);
 3,5-bis((3,5-di-tert-butyl-4-hydroxy)benzyl)-2,4,6-trimethylphenol;
 pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl) propionate;
 calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate);
 o,o-dimethyl o-(4-cyanophenyl) phosphorothioate;
 terephthalic acid, 1,4-dithio-,S,S-bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) ester;
 triethylene glycol bis(3-tert-butyl-4-hydroxy-5-methylhydrocinnamate);
 hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate);
 1,2-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide;
 4,4'-di-tert-octyldiphenamine;
 phosphonic acid, (3,5-di-tert-butyl-4-hydroxybenzyl)-,dioctadecyl ester;
 1,3,5-trimethyl-2,4,6-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)benzene;
 2,4-bis(octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine;
 isooctyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate;
 octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate;
 3,7-bis(1,1,3,3-tetramethylbutyl)-10H-phenothiazine;
 2,2'-methylenebis(4-methyl-6-tert-butylphenol)monoacrylate;
 2-tert-butyl-6-[1-(3-tert-butyl-2-hydroxy-5-methylphenyl)ethyl]-4-methylphenyl acrylate;
 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate;
 1,3-dihydro-2H-Benzimidazole;
 2-methyl-4,6-bis[(octylthio)methyl]phenol;
 N,N'-trimethylenebis-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionamide];
 4-n-octadecyloxy-2,6-diphenylphenol;
 2,2'-ethylidenebis[4,6-di-tert-butylphenol] ;
 N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide);

diethyl (3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate ;
 4-octyl-N-(4-octylphenyl)-benzenamine;
 4,4'-di-tert-octyldiphenylamine;
 N-phenyl-1-naphthalenamine;
 2,2,4-trimethyl-1,2-dihydroquinoline polymer;
 tris[2-tert-butyl-4-(3-ter-butyl-4-hydroxy-6-methylphenylthio)-5-methyl
 phenyl] phosphite ;
 zinc dinonyldithiocarbamate;
 and
 3,9-bis[1,1-diimethyl-2-[(3-tert-butyl-4-hydroxy-5-
 methylphenyl)propionyloxy]ethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane.

6. The heat stabilizing composition of claim 1, wherein said sulfur-containing
 secondary stabilizer is selected from the group consisting of 2,2'-thiobis(4-
 methyl-6-tert-butylphenol);
 tetrakis(3-laurylthiopropionyloxymethyl)methane;
 pentaerythritol tetrakis(3-alkylthiopropionate) wherein alkyl is C₆₋₂₀ carbon
 atoms, e.g. pentaerythritol tetrakis(3-dodecylthiopropionate);
 lauryl 3,3'-thiodipropionate;
 stearyl 3,3'-thiodipropionate;
 distearyl disulfide;
 dilauryl 3,3'-thiodipropionate;
 dimyristyl 3,3'-thiodipropionate;
 propionic acid, 3,3'-thiobis-, didodecyl ester;
 ditridecyl 3,3'-thiodipropionate;
 distearyl 3,3'-thiodipropionate ,
 dioctadecyl 3,3'-thiodipropionate; and
 dimyristyl 3,3'-thiodipropionate.

7. The heat stabilizing composition of claim 1, wherein said sulfur-containing secondary stabilizer is selected from the group consisting of 2,2'-thiobis(4-methyl-6-tert-butylphenol);
 tetrakis(3-laurylthiopropionyloxymethyl)methane;
 pentaerythritol tetrakis(3-alkylthiopropionate) wherein alkyl is C₆₋₂₀ carbon atoms, e.g. pentaerythritol tetrakis(3-dodecylthiopropionate);
 lauryl 3,3'-thiodipropionate;
 stearyl 3,3'-thiodipropionate;
 distearyl disulfide;
 dilauryl 3,3'-thiodipropionate;
 dimyristyl 3,3'-thiodipropionate;
 propionic acid, 3,3'-thiobis-, didodecyl ester;
 ditridecyl 3,3'-thiodipropionate;
 distearyl 3,3'-thiodipropionate ,
 dioctadecyl 3,3-thiodipropionate; and
 dimyristyl 3,3'-thiodipropionate.

8. The heat stabilizing composition of claim 1, wherein said hindered amine has the structure:



in which n and m are independently 0 to 100, with the proviso that n and m cannot both be 0,
 R1 is hydrogen, C₅-C₇-cycloalkyl, or a C₁-C₁₂-alkyl group,

R^2 and R^3 independently of one another are a hydrogen atom or a C_1 - C_{18} -alkyl group or, together with the carbon atom connecting them, a 5- to 13-membered hindered amino group, and

R^4 is either hydrogen or a C_1 - C_5 -alkyl group, an oxygen radical O^* , $-OH$, $-NO$, $-CH_2CN$, benzyl, allyl, a C_1 - C_{10} -alkyloxy group, a C_5 - C_6 -cycloalkyloxy group, a C_6 - C_7 -aryloxy group in which additionally the aryl radical can also be substituted, a C_7 - C_{10} -arylalkyloxy group in which additionally the aryl radical can also be substituted, a C_3 - C_6 -alkenyl group, a C_3 - C_6 -alkynyl group, a C_1 - C_4 -acyl group, halogen or C_7 - C_9 -phenylalkyl which is unsubstituted or substituted on the phenyl ring by C_1 - C_2 -alkyl.

9. The heat stabilizing composition of claim 1 further comprising a benzophenone compound.

10. The heat stabilizing composition of claim 1, further comprising carbon black pigment.

11. A polyolefin compound comprising:

at least one polyolefin resin; and

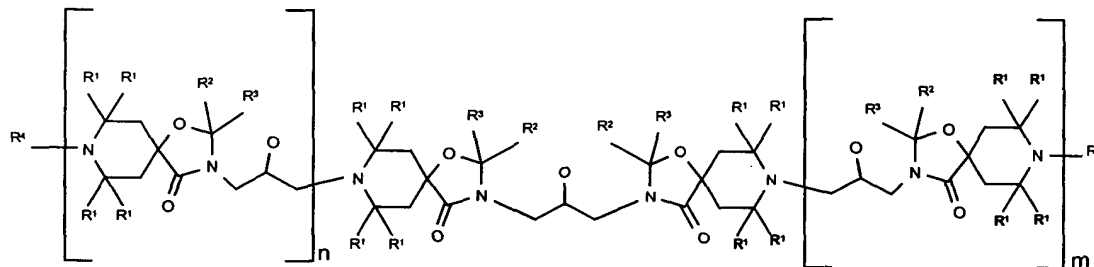
a heat stabilizing compound including:

- (A) an oxidized, non-cationized, non-silylated sulfur black pigment,
- (B) a hindered phenolic antioxidant,
- (C) a sulfur-containing secondary stabilizer, and
- (D) a hindered amine.

12. The polyolefin compound of claim 11, wherein said at least one polyolefin resin is selected from homopolymers of polyethylene, polypropylene, poly-1-butene, polyisobutene, poly-3-methyl-1-butene, poly-4-methyl-1-pentene, and cyclic polyolefin.

13. The polyolefin compound of claim 11, wherein (A) is selected from C. I. Sulphur Black 1; C. I. Sulphur Black 2; C. I. Sulphur Black 11; and C. I. Sulphur Black 18.

14. The polyolefin compound of claim 11, wherein said hindered amine has the structure:



in which n and m are independently 0 to 100, with the proviso that n and m cannot both be 0,

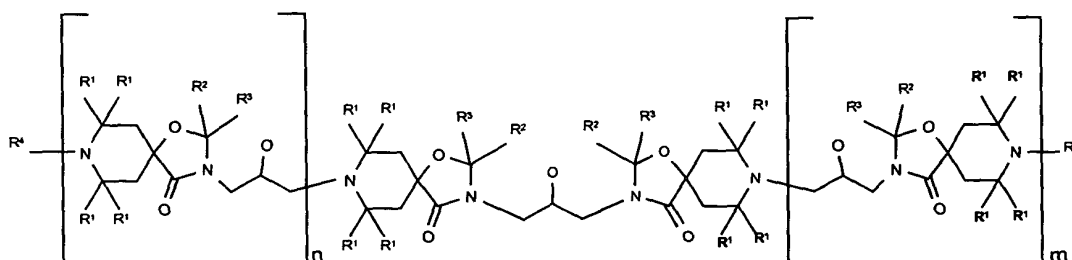
R¹ is hydrogen, C₅-C₇-cycloalkyl, or a C₁-C₁₂-alkyl group,

R² and R³ independently of one another are a hydrogen atom or a C₁-C₁₈-alkyl group or, together with the carbon atom connecting them, a 5- to 13-membered hindered amino group, and

R⁴ is either hydrogen or a C₁-C₅-alkyl group, an oxygen radical O*, -OH, -NO, -CH₂CN, benzyl, allyl, a C₁-C₁₀-alkyloxy group, a C₅-C₆-cycloalkyloxy group, a C₆-C₇-aryloxy group in which additionally the aryl radical can also be substituted, a C₇-C₁₀-arylalkyloxy group in which additionally the aryl radical can also be substituted, a C₃-C₆-alkenyl group, a C₃-C₆-alkynyl group, a C₁-C₄-acyl group, halogen or C₇-C₉-phenylalkyl which is unsubstituted or substituted on the phenyl ring by C₁-C₂-alkyl.

15. The polyolefin compound of claim 11, wherein said heat stabilizing compound further comprises carbon black pigment.

16. The polyolefin compound of claim 11, wherein said sulphur black pigment is washed to reduce the water soluble salts present in said sulphur black pigment.
17. A dry-blended, melt-phase compounded polyolefin article comprising the polyolefin compound of claim 11.
18. A dry-blended, melt-phase compounded polyolefin article comprising the polyolefin compound of claim 15.
19. A method for increasing the long term heat aging stability of a polyolefin resin comprising the steps of adding to the polyolefin resin, (A) an oxidized, non-cationized, non-silylated sulfur black pigment, (B) a hindered phenolic antioxidant, (C) a sulfur-containing secondary stabilizer, and (D) a hindered amine.
20. The method of claim 19, wherein (A) is selected from C. I. Sulphur Black 1; C. I. Sulphur Black 2; C. I. Sulphur Black 11; and C. I. Sulphur Black 18.
21. The method of claim 19, wherein (A) is added in an amount in the range from 0.1 to 10 w% on total wt%, (B) from 0.01 to 1. w% on total wt.%, (C) from 0.02 to 2 w% on total wt%, and (D) is from 0.05-1 w% on total w%.
22. The method of claim 19, wherein said hindered amine has the structure:



in which n and m are independently 0 to 100, with the proviso that n and m cannot both be 0,

R¹ is hydrogen, C₅-C₇-cycloalkyl, or a C₁-C₁₂-alkyl group,

R² and R³ independently of one another are a hydrogen atom or a C₁-C₁₈-alkyl group or, together with the carbon atom connecting them, a 5- to 13-membered hindered amino group, and

R⁴ is either hydrogen or a C₁-C₅-alkyl group, an oxygen radical O*, -OH, -NO, -CH₂CN, benzyl, allyl, a C₁-C₁₀-alkyloxy group, a C₅-C₆-cycloalkyloxy group, a C₆-C₇-aryloxy group in which additionally the aryl radical can also be substituted, a C₇-C₁₀-arylalkyloxy group in which additionally the aryl radical can also be substituted, a C₃-C₆-alkenyl group, a C₃-C₆-alkynyl group, a C₁-C₄-acyl group, halogen or C₇-C₉-phenylalkyl which is unsubstituted or substituted on the phenyl ring by C₁-C₂-alkyl.

23. The method of claim 19, further comprising adding carbon black pigment to the polyolefin resin.

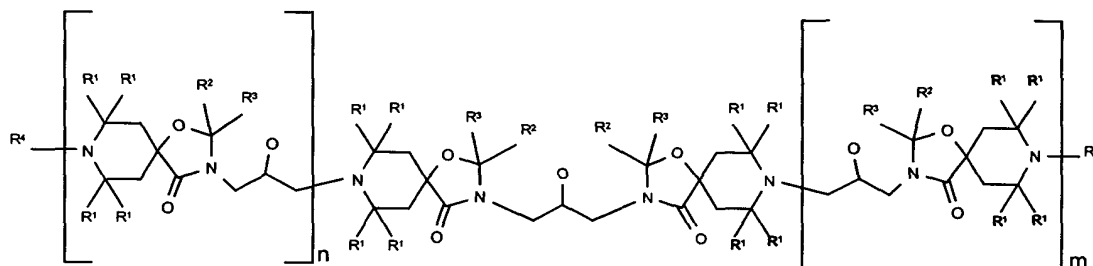
24. A method for increasing the long term heat aging stability of a polyolefin resin comprising the steps of:

reducing the concentration of water soluble salts in a sulfur black pigment to form a treated sulfur black pigment; and

adding said treated sulfur black pigment, a hindered phenolic antioxidant, a sulfur-containing secondary stabilizer, and a hindered amine to the polyolefin resin.

25. The method of claim 24, wherein the sulfur black pigment is selected from C. I. Sulphur Black 1; C. I. Sulphur Black 2; C. I. Sulphur Black 11; and C. I. Sulphur Black 18.

26. The method of claim 24, wherein said hindered amine has the structure:



in which n and m are independently 0 to 100, with the proviso that n and m cannot both be 0,

R¹ is hydrogen, C₅-C₇-cycloalkyl, or a C₁-C₁₂-alkyl group,

R² and R³ independently of one another are a hydrogen atom or a C₁-C₁₈-alkyl group or, together with the carbon atom connecting them, a 5- to 13-membered hindered amino group, and

R⁴ is either hydrogen or a C₁-C₅-alkyl group, an oxygen radical O*, -OH, -NO, -CH₂CN, benzyl, allyl, a C₁-C₁₀-alkyloxy group, a C₅-C₆-cycloalkyloxy group, a C₆-C₇-aryloxy group in which additionally the aryl radical can also be substituted, a C₇-C₁₀-arylalkyloxy group in which additionally the aryl radical can also be substituted, a C₃-C₆-alkenyl group, a C₃-C₆-alkynyl group, a C₁-C₄-acyl group, halogen or C₇-C₉-phenylalkyl which is unsubstituted or substituted on the phenyl ring by C₁-C₂-alkyl.

27. The method of claim 24, further comprising adding carbon black to the polyolefin resin.

28. The method of claim 24, wherein said reducing step further comprises washing said sulphur black pigment.

29. A masterbatch composition comprising:

a polyolefin carrier;

a heat stabilizing composition including

(A) an oxidized, non-cationized, non-silylated sulfur black pigment,

(B) a hindered phenolic antioxidant,

(C) a sulfur-containing secondary stabilizer, and

(D) a hindered amine.

30. The masterbatch composition of claim 29, wherein said heat stabilizing composition is present in an amount between 20% and 50% by weight.